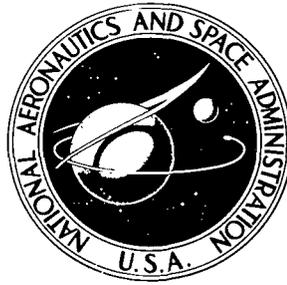


NASA TECHNICAL NOTE



NASA TN D-5441

NASA TN D-5441

LOAN COPY: RETURN TO
APC L (WHL-2)
KIBLER AFB, N ME



**ABSORPTION OF HYDROGEN BY PALLADIUM
AND ELECTRICAL RESISTIVITY UP TO
HYDROGEN-PALLADIUM ATOM RATIOS OF 0.97**

by Dumas A. Otterson and Robert J. Smith

Lewis Research Center

Cleveland, Ohio



0132067

1. Report No. NASA TN D-5441	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle ABSORPTION OF HYDROGEN BY PALLADIUM AND ELECTRICAL RESISTIVITY UP TO HYDROGEN-PALLADIUM ATOM RATIOS OF 0.97		5. Report Date September 1969	6. Performing Organization Code
7. Author(s) by Dumas A. Otterson and Robert J. Smith	8. Performing Organization Report No. E-5158		10. Work Unit No. 129-03
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Note	
15. Supplementary Notes		14. Sponsoring Agency Code	
16. Abstract <p>The electrical resistivity of the palladium-hydrogen system (PdH_x) was measured to a H/Pd atom ratio x of 0.97 at 4.2 and 273 K. The Bambakidis, Smith, and Otterson model proposed for the palladium-deuterium system (PdD_x) is applied to PdH_x. The model is used to explain the concentration dependence of the peak in resistivity as a function of temperature near 50 K and the concentration dependence in the resistivity scatter due to quench rate observed at 4.2 K. The present results are virtually independent of hydrogen isotope effects. Techniques used to attain values of x up to 0.97 are given. Hydrogen retention by these specimens is discussed.</p>			
17. Key Words (Suggested by Author(s))		18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 17	22. Price* \$3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

ABSORPTION OF HYDROGEN BY PALLADIUM AND ELECTRICAL RESISTIVITY UP TO HYDROGEN-PALLADIUM ATOM RATIOS OF 0.97

by Dumas A. Otterson and Robert J. Smith

Lewis Research Center

SUMMARY

The electrical resistivity of the palladium-hydrogen system (PdH_x) was measured up to a H/Pd atom ratio x of 0.97 at temperatures of 4.2 and 273 K. The model which Bambakidis, Smith, and Otterson proposed for the palladium-deuterium system is applicable to the palladium-hydrogen system. The model can be used to explain (1) the concentration dependence of the peak in resistivity as a function of temperature near 50 K and (2) the concentration dependence of the scatter in resistivity due to quench rate from 273 to 4.2 K. The present results are virtually independent of the isotope involved. The techniques used to attain values of x up to 0.97 are discussed. Hydrogen retention of such specimens is also briefly covered.

INTRODUCTION

Bambakidis, Smith, and Otterson (ref. 1) recently proposed a model to explain the structural portion of the relation between electrical resistivity and deuterium (D) concentration in palladium (Pd). The model explains data obtained at 4.2 and 273 K. The D/Pd atom ratio x ranged from approximately 0.2 to 0.90.

At 273 K, an almost linear relation exists between the resistivity and the deuterium (or hydrogen) concentration x in palladium, for x less than 0.7. In this concentration region at 4.2 K, the relation has a much greater curvature away from the concentration axis for PdD_x . To explain this difference, it was necessary to assume that the deuterium ions were at least partially screened from the conduction electrons at 4.2 K for x less than 0.55. As x increased from 0.55 to 1, Bambakidis, Smith, and Otterson assumed two interpenetrating face-centered cubic lattices (NaCl type structure) with vacancies being filled in the deuterium lattice. Thus, we obtain the maximum and the subsequent decrease in resistivity as x approaches 0.90. The model predicts that the resistivity should continue to decrease as x approaches 1.

Hydrogen is generally considered to be electronically the same as deuterium. However, some differences in results for the two systems have been observed in the relation between resistivity and temperature (refs. 2 and 3) and in neutron diffraction experiments (refs. 2 and 4). In both PdH_x and PdD_x where x is close to 0.6, a resistivity maximum is found near 50 K (refs. 2 and 3). However, $\text{PdD}_{0.6}$ required much more time for its resistivity to become constant than $\text{PdH}_{0.6}$ after cooling to a temperature near 50 K. Neutron diffraction experiments by Ferguson, Schindler, Tanaka, and Morita (ref. 4) revealed that, near 50 K, some hydrogen had moved from interstitial octahedral sites (0, 0, 1/2; 1/2, 0, 0; . . .) of the palladium lattice to the tetrahedral sites (1/4, 1/4, 1/4; 3/4, 3/4, 3/4; . . .) (O-T transitions). These O-T transitions are used to explain the peak in the curve of resistivity as a function of temperature near 50 K for x between 0.48 and 0.70 (refs. 3 to 5). Also these transitions may be used to explain the peak in the curve of specific heat as a function of temperature near 50 K for x between 0.125 and 0.75 (refs. 4 and 6). However, the neutron diffraction results for $\text{PdD}_{0.6}$ could not be definitely interpreted in terms of O-T transitions even though diffraction pattern changes occurred. (In a private communication, Schindler expressed the opinion that O-T transitions in PdD_x might have been seen if the specimen had been kept at 50 K for a minimum of 4 hr prior to the neutron diffraction study.)

Therefore, the authors decided to study the PdH_x system at 4.2 and 273 K to determine if isotopic differences existed in the structural resistivity data for PdH_x and PdD_x . The published resistivity as a function of hydrogen concentration for PdH_x is limited to concentrations up to x equal to 0.88 and to temperatures above 273 K (refs. 7 and 8, p. 55). However, the authors have developed techniques to attain H/Pd atom ratios greater than 0.90. This new information permits the testing of the Bambakidis-Smith-Otterson model to almost $\text{PdH}_{1.0}$ and lends added support to the arguments for the dependency of the resistivity on vacancies in the NaCl structured Pd-H.

The techniques involved in charging palladium with hydrogen to H/Pd atom ratios in excess of 0.9 are felt to be of significant interest to others in the field. Therefore, the charging procedure and hydrogen retention are discussed in detail in this report.

EXPERIMENTAL

The experimental work involved specimen preparation, resistance measurements, the determination of the hydrogen content of the specimens, and tests to indicate the retention of hydrogen in PdH_x .

Specimen Preparation

Treatment of specimen prior to charging. - The palladium wires used in this work were 0.254 millimeter in diameter. The manufacturer stated that the impurity concentration, including interstitials, was less than 0.01 percent. The wires were annealed by joule heating to 900° C in a vacuum of 5.0×10^{-8} torr (7×10^{-6} N/m²). The wires were cut to about 8-centimeter lengths, rinsed in acetone, and then in chloroform. Next, they were soaked several minutes in concentrated hydrochloric acid. They were finally rinsed with distilled water just before being placed in the electrolysis cell for the electrolytic preparation of PdH_x.

Electrolytic charging with hydrogen. - In the most successful modification of the charging procedure, electrolysis was carried out in a 250-cubic-centimeter beaker using a graphite anode and the palladium specimen as the cathode. The anode, two high-purity spectrographic grade 3/16-inch- (0.48-cm-) diameter rods, was placed in a porous battery cup. The cup was 1 inch (2.54 cm) in outside diameter and 3 inches (7.62 cm) tall. It had 1/8-inch- (0.32-cm-) thick walls. One cubic centimeter of formalin (40 percent formaldehyde) was added to the cup prior to adding electrolyte. The electrolyte was about 250 cubic centimeters of 0.1 normal sulfuric acid containing 0.25 gram of photographic grade sodium sulfide flakes. In general, the charging current density was about 8 milliamperes per square centimeter. The charging periods were as long as 18 hours. Other less successful modifications of the charging procedure involved the use of various anode materials, cell configurations, and electrolytes.

Because oxidizing agents were sometimes detected in the electrolyte, the electrolytes were often tested for hydrogen peroxide and a peroxysulfate. The test for hydrogen peroxide consisted of adding 1 cubic centimeter of a dilute acidic solution of tetravalent titanium (about 1 molar) to about 10 cubic centimeters of electrolyte. If the mixture turned yellow, peroxide was indicated. If no peroxide was indicated, the following test was used for peroxysulfate. Equal volumes of the electrolyte, reagent grade hydrochloric acid, and a solution containing 0.1 percent (by weight) of tolidine in 0.1 normal hydrochloric acid were mixed and heated. The formation of a yellow color in the hot solution indicated a peroxysulfate (most probably persulfate).

Resistance Measurements

Technique. - The resistance measurements were made at 4.2 and 273 K on the annealed specimens before and after hydrogen absorption. We used the conventional four-probe potentiometric technique. A constant current source with a stability of 0.001 percent and a potentiometer with an accuracy of 0.001 percent and capable of measuring

10^{-8} volt were used. The current was 10 milliamperes for all measurements. This current was determined by measuring the potential drop across a 1-ohm standard resistor having an accuracy of 0.01 percent. We estimate the error in resistance measurement to be about 0.01 percent.

The resistivity data are presented in terms of the resistivity ratio ρ_x/ρ_0 . The resistivity of the annealed palladium specimen at 4.2 or 273 K is ρ_0 . The resistivity of the same section of the specimen at the same temperature after hydrogen absorption is ρ_x .

Specimen holder. - The specimen holder was a phenoformaldehyde board (0.18 by 7 cm by 5.5 cm) designed to permit rapid quenching. The connections to the specimen were made mechanically through phosphor bronze contacts. Five potential contacts were spaced about 1 centimeter apart on the board. Holes, slightly less than 1 centimeter in diameter, were drilled through the board between the contact points to permit intimate contact of the specimen with liquid helium. Because resistance readings could be obtained for four sections of the specimen, some of the hydrogen concentration gradients along the specimens could be detected. With this holder, the temperature of the board could be reduced from 273 to 4.2 K in about 8 ± 2 seconds. In preliminary work more massive holders were used; as much as 30 seconds were needed to quench a specimen with these holders.

Determination of Hydrogen in the Specimen

For determination of the H/Pd atom ratios x , each specimen was sectioned into four 1-centimeter pieces that corresponded to the spacing of the potential contact positions on the specimen holder. Within 1/4 hour after completing the resistance measurements, each specimen was either immersed in liquid nitrogen (for subsequent chemical analysis) or placed directly into an analysis chamber from which the air was immediately evacuated. After evacuation to about 10^{-6} torr (1.4×10^{-4} N/m²), the hydrogen was removed by heating separately each 1-centimeter section for 1/4 hour at 573 K in the isolated evacuated system. The hydrogen was expanded into and determined by a mass spectrometer that was capable of 1 percent precision. This precision was achieved by determining the sensitivity of the mass spectrometer to hydrogen gas every day. The only results that were used were those obtained when the sensitivity did not change by more than 1 percent from the previous day. In addition, the expansion system of the mass spectrometer was calibrated using a precisely known number of micromoles of gas. The completeness of hydrogen removal from the specimen under these conditions was tested by determining the amount of hydrogen that could be removed in a subsequent gas collection at 100° above the initial collection temperature. The specimens (usually about 6 mg) were then weighed to three significant figures.

Techniques for Study of Hydrogen Retention in Palladium-Hydrogen

When the H/Pd atom ratio exceeds 0.7 for a specimen stored at room temperature, the hydrogen tends to evolve. We therefore tried to determine the error arising from the time lapse between the resistivity measurement and the hydrogen determination of the specimen. The retention was studied by two methods: one based on the direct determination of hydrogen content and an indirect method based on the change in resistivity of the specimen (function of the hydrogen concentration) with time. The direct method could be used to study the change in hydrogen content due to aging in any medium and at any temperature. The retention was tested at 77 K (in liquid nitrogen) and at room temperature in air, water, electrolyte, and vacuum. The indirect method was limited to study of the retention in water at 273 K and liquid nitrogen. The results from the direct method were more erratic than those of the indirect method. The direct method required the assumption that the specimen was evenly charged along its length while the indirect method did not.

HYDROGEN ABSORPTION BY PALLADIUM

Results of Charging Process Studies

Achievement of high concentrations. - The charging process as described was found to be effective in producing PdH_x with x greater than 0.9. Values as high as 0.97 could generally be attained in about 2 hours. The preliminary experiments showed that the presence of several types of substances in the electrolyte inhibited the production of high H/Pd atom ratios by virtue of their reduction at the PdH_x electrode. These substances might be added to the electrolyte from impure reagents, the anode partially dissolving, or oxidants being formed at the anode.

Selection of anode material. - Certain metallic anodes (such as copper, gold, and nickel) were found to be unusable. These metallic anodes dissolved slowly and plated out on the cathode. This plating slowed or stopped the absorption process. Platinum and palladium anodes were not used because of the considerable effort that would have been required to determine whether any anodic material had transferred to the cathode. The difficulty with aluminum was still more subtle. Aluminum became anodized in acid solution and therefore dissolved very slowly. Emission spectrographic analysis indicated that no aluminum plated out on the PdH_x cathode; however, the possibility existed that impurities in the aluminum can dissolve and be reduced at the cathode. Although iron was never used as an anode, several times the presence of iron was detected on dis-

colored cathodes. Thus, spectrographic grade graphite, being free of these side effects, was found to be the most suitable anode.

Effect of anodically formed oxidants. - The preliminary tests also showed that at least two oxidants were formed even at the graphite anode. The presence of hydrogen peroxide was detected in the electrolyte after extended periods of electrolysis, primarily in the anode chamber. Occasionally, a peroxy sulfate was found instead of hydrogen peroxide. Such oxidants could prevent the formation of a high H/Pd atom ratio if they accumulated at the cathode. Neither oxidant was found in the electrolyte that had been used less than several hours. The effects of these oxidants were minimized by always (1) using fresh electrolyte, (2) using a porous cup to slow down diffusion between the anode and cathode, and (3) adding formaldehyde (a reducing agent) to the anode chamber. The effectiveness of these three techniques was substantiated as described in the following paragraph.

When electrolytic charging of palladium is studied as a function of the duration of charging, the resulting curves generally showed features similar to those in figure 1;

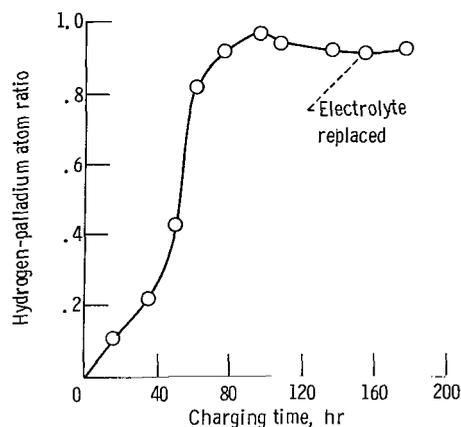


Figure 1. - Electrolytic charging of palladium. Electrolyte, 0.1 normal sulfuric acid solution with formaldehyde.

namely, as electrolysis proceeds, The H/Pd atom ratio x increases rapidly, levels off, and then begins to decrease with time. All charging procedures that continued long enough generally showed these features even though the charging rates were different. Even with apparently identical procedures, the charging rate varied somewhat from specimen to specimen. Anodically formed oxidants were generally found in the electrolyte after x showed a decrease. When the electrolyte was replaced, an increase in x with additional charging could be detected. When both the porous cup and formaldehyde were used, the

value of x remained at the maximum for a much longer charging period. Indeed, this period was about 18 hours with formaldehyde present. Without formaldehyde, this period may be less than 1 hour.

The described features are found in figure 1. Figure 1 presents x plotted against time for electrolytic charging of palladium according to the recommended procedure except that no formaldehyde was present. The rate of hydrogen absorption was usually higher with higher current densities, but the maximum value of x that could be attained was generally less.

Results of Hydrogen Retention Studies

The work presented in this section was designed to test a necessary assumption; namely, the measured value of x was the value when the resistance measurement was made. In general, the work indicated (1) that virtually no hydrogen was lost in PdH_x upon aging up to 36 hours in liquid nitrogen and (2) that less than 2 percent of the hydrogen is lost upon aging 1/4 hour near room temperature in air or water.

Observations based on direct hydrogen determinations. - Mass spectrographic determination of hydrogen was based on the assumption that the hydrogen concentration along the specimen was constant. This was not always true, and so the results were somewhat variable. However, several observations can be made. The rate of loss of hydrogen in vacuum, water, or fresh electrolyte was generally found to be slightly less than that in air with no rate more than 2 percent per 1/4 hour. However, hydrogen was completely lost within 48 hours if the specimen was stored in electrolyte containing hydrogen peroxide. The peroxide could be either formed anodically or added to fresh electrolyte as stabilized reagent grade hydrogen peroxide. For example, in one instance, peroxide was detected when electrolysis was terminated and the aging began. The H/Pd atom ratio was about 0.86. After 3 days, no peroxide could be detected in the electrolyte and no hydrogen was found in the specimen. In contrast, on numerous occasions portions of specimens stored overnight in liquid nitrogen showed the same hydrogen content as other portions analyzed immediately.

Observations based on resistivity measurements. - Typical results obtained from observing the change of ρ_x/ρ_0 with the time a specimen is aged in water at 273 K are shown in figure 2. Direct analysis indicated that x equaled 0.86 initially and 0.66 at the end of the test. If one uses the relation between resistivity and concentration (fig. 4, p. 11), which is presented and discussed in detail in the section EFFECT OF HYDROGEN CONCENTRATION ON RESISTIVITY OF PALLADIUM-HYDROGEN, one can estimate the rate of hydrogen loss from figure 2. Upon referring to figure 4, one can interpret figure 2 as follows: the initial rise in ρ_x/ρ_0 represents a decrease in x from about 0.86 to 0.75. In the region of the maximum, x can decrease with no detectable change

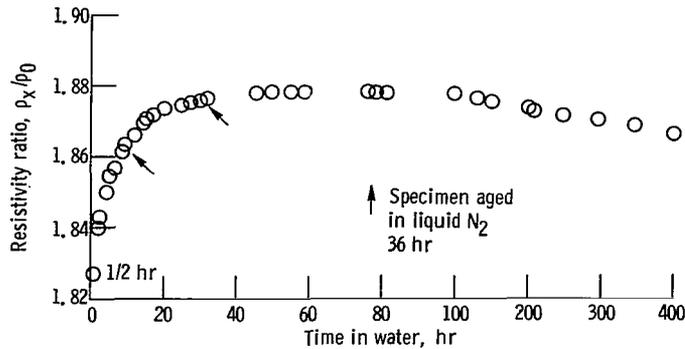


Figure 2. - Change in resistivity ratio for PdH stored in water at 273 K. Hydrogen-palladium atom ratio: initial, ≈ 0.86 ; final, ≈ 0.66 .

in ρ_x/ρ_0 . The subsequent decrease in ρ_x/ρ_0 also represents a decrease in x from about 0.70 to 0.66. In other words, figure 2 represents a continual loss of hydrogen. It should be noted that the change in ρ_x/ρ_0 for the first 10 hours suggests that the decrease in x would be less than 0.07 (or less than 0.01 during the first 1/2 hr of aging).

Referring again to figure 2, the arrows indicate periods of aging in liquid nitrogen of at least 36 hours. It is quite obvious that no detectable loss of hydrogen resulted. The stability in liquid nitrogen allows us to store samples of PdH $_x$ after the resistance measurements without increasing the error in the hydrogen determination.

Comparison of Electrolytic Method With Absorption From Hydrogen Gas

At standard conditions, considerably higher concentrations of hydrogen can be absorbed by palladium by electrolytic techniques than by absorption from the gas. With our electrolytic technique, H/Pd atoms ratios as high as 0.97 were attained, while pressure-concentration relations (ref. 8, p. 21) indicate that a H/Pd atom ratio of only 0.72 can be attained by absorption from the gas at 273 K and 1 atmosphere (1.01×10^5 N/m 2) pressure. Furthermore, these relations also indicate that hydrogen must be in excess of 1000 atmospheres (1.01×10^8 N/m 2) in order for x to exceed 0.9. We do not expect to have hydrogen at 1000 atmospheres (1.01×10^8 N/m 2) as the result of electrolysis in a cell open to the atmosphere. Therefore, we believe another variable is the cause for the enhanced hydrogen absorption attained with cathodic deposition.

One may postulate that this variable is the hydrogen atom concentration in the absorbed layer. Andrews and Ubbelohde's (ref. 9) work implied that a high concentration of hydrogen atoms in the adsorbed layer would lead to a hydrogen concentration in the specimen in excess of the value in equilibrium with the gas. It is generally believed

that cathodic deposition of hydrogen from an acid solution produces adsorbed hydrogen atoms initially on the cathode; because of this, the catalytic activity of the surface, which influences the adsorbed atom concentration, can also be expected to affect the absorption process. On a catalytically active surface, the rate of association of hydrogen atoms to molecular hydrogen would be rapid. Hence, the hydrogen atom concentration would be less on the catalytically active surface than on an inactive one. Moreover, the concentration of hydrogen that can be absorbed by a catalytically active surface would be less than that of an inactive surface. It should be noted that the adsorbed hydrogen may be composed of either a simple atom or a hydrogen ion and an electron which are far enough apart to be considered separate entities.

Lewis (ref. 8, p. 68) reported that palladium cathodes with "bright" or "smooth" surfaces generally have low catalytic activity. And the amount of hydrogen that can be absorbed as the result of electrolysis may substantially exceed the amount absorbed by palladium with catalytically active surfaces. In our work, we observed that values of x in excess of 0.95 could only be prepared consistently if sulfide ion was present in the electrolyte. Sulfide ion is generally believed to be a catalytic poison for the recombination of hydrogen atoms on a metallic surface (ref. 10). Therefore, we believe that the catalytic activity of the palladium cathodes in the presence of sulfide ion was consistently very low, which resulted in high values of x .

The role of adsorbed hydrogen atoms in hydrogen absorption by palladium is further elucidated by another observation by Lewis (ref. 8, p. 97); that is, catalytic poisons (such as certain compounds of sulfur and arsenic) are shown to hinder the absorption of hydrogen from the gas by palladium. This effect can be understood if hydrogen is absorbed by palladium as atoms but not molecules. The hydrogen adsorbed on the palladium surface from the gas has at most a low concentration of atoms. Hydrogen absorption would remove the atoms from the surface which must be replaced for absorption to continue. If the surface is catalytically inactive (i. e., poisoned) the rate of dissociation of hydrogen molecules would be slow. Hence, the rate of hydrogen absorption would be slow, as was indicated by Lewis. Thus, support is given to the viewpoint that hydrogen atoms but not hydrogen molecules are absorbed by palladium.

We can summarize our mechanism for hydrogen absorption by palladium as follows: Hydrogen atoms but not molecules are absorbed by palladium from the adsorbed layer. The concentration of hydrogen absorbed in the palladium is a function of the hydrogen atom concentration in the adsorbed layer, which is a function of the rate at which the atoms are replaced in the adsorbed layer. This aspect of the mechanism is equally applicable to high temperature gaseous charging as well as electrolytic charging.

Results of Resistivity Measurements and Discussion of Scatter

Figures 3 and 4 present ρ_x/ρ_0 plotted against H/Pd atom ratio for 4.2 and 273 K. At 4.2 K, ρ_x/ρ_0 shows little change up to x approximately 0.36. As x increases above 0.36, ρ_x/ρ_0 increases more rapidly and reaches a peak value of 116 for x approximately 0.70. Then ρ_x/ρ_0 decreases to about 45 for x equal to 0.97. At 273 K (fig. 4) ρ_x/ρ_0 increases almost linearly for x between 0.02 and 0.70. Between 0.7 and 0.8 ρ_x/ρ_0 reaches a maximum value of 1.9 and then decreases to about 1.35 for x approximately 0.97. A rapid change in the slope of the curve occurs for x less than 0.02. This "knee" has been reported by others and is attributed to the start of the β -phase for increasing x (ref. 8, p. 50).

The errors in resistance measurements and determinations of x cannot account for the scatter in the data of figures 3 and 4. One source of error would be the presence of hydrogen in voids. This hydrogen does not necessarily influence the resistivity but is included in the measured value of x . Hence, for a given ρ_x/ρ_0 value, the lowest value of x in a given portion of the envelope of data points is felt to be the most representative of the hydrogen concentration in the palladium lattice.

In the region of the maximum, an additional systematic error arises. Here the lower values of ρ_x/ρ_0 for a given value of x may be in error because of uneven distribution

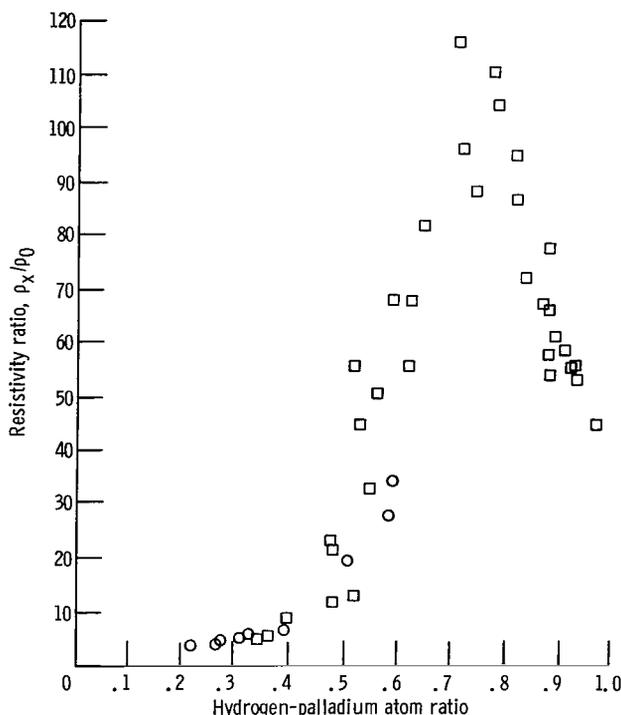


Figure 3. - Resistivity ratio as function of hydrogen-palladium atom ratio at 4.2 K. Resistivity at 4.2 K (annealed prior to absorption), ρ_0 ; resistivity after absorption, ρ_x .

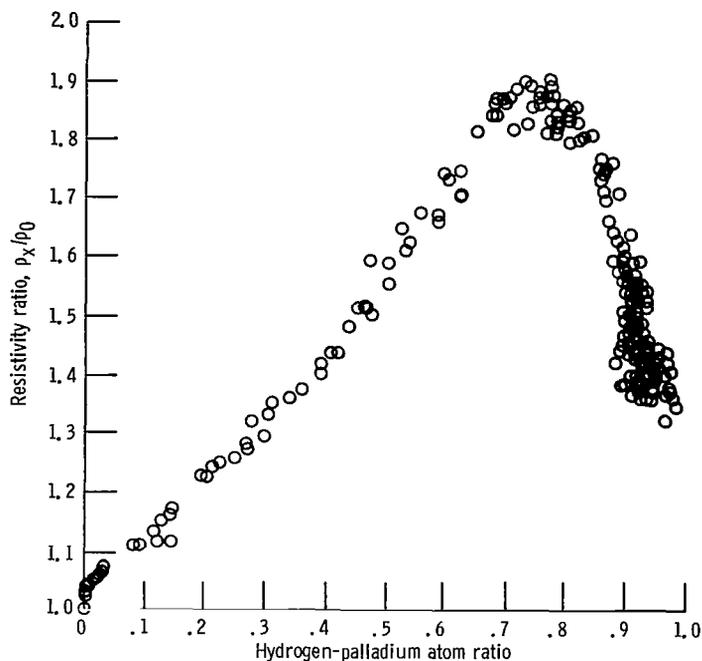


Figure 4. - Resistivity ratio as function of hydrogen-palladium ratio at 273 K. Resistivity at 273 K (annealed prior to absorption, ρ_0 ; resistivity after absorption, ρ_x .

of hydrogen along the PdH_x lattice specimen. This effect of uneven distribution can be understood if we remember that the measured values of x and ρ_x/ρ_0 are the averages of those of each tiny segment of the 1-centimeter section. A section containing a segment with x less than that at the peak and another with x greater than that at the peak would show a ρ_x/ρ_0 less than the peak value because the values of ρ_x/ρ_0 for both segments would be less than the maximum. This reasoning associates the higher ρ_x/ρ_0 values with the least error.

In the data for x greater than 0.36 in figure 3, the scatter appears the greatest. We attribute some of this scatter to a possible difference in quench rates from 273 to 4.2 K for the specimens used. The quench rates could differ by as much as 40 percent (8 ± 2 sec). It is possible that some O-T transitions (or $\beta \rightarrow \beta^*$) occurred. Haywood and Verdini (ref. 5) reported that these transitions are time dependent.

Comparison of the Bambakidis-Smith-Otterson Model With the Palladium-Hydrogen System

The model in terms of palladium-hydrogen. - The results obtained for the PdH_x system are consistent with the model proposed for the PdD_x system by Bambakidis, Smith, and Otterson (ref. 1). The curves at 4.2 and 273 K for ρ_x/ρ_0 as a function of x (figs. 3 and 4) are quite similar to those for PdD_x . The values of x at which inflections occur are almost the same for both systems. The main difference is that the maximum value for ρ_x/ρ_0 is somewhat lower for PdH_x than for PdD_x . This difference may be associated with the fact that ions of these two hydrogen isotopes have different masses and spins. However, for x less than 0.36 at 4.2 K, ρ_x/ρ_0 values are essentially equal.

The model is now briefly summarized in terms of the PdH_x system. As hydrogen is added to palladium, its electron first enters holes in the d-band of the palladium lattice. Vuillemin has deduced from deHaas-vanAphen experiments that pure palladium has 0.36 hole in its d-band (ref. 11). Presumably, the lattice expansion, caused by the hydrogen absorption, and the presence of interstitial hydrogen ion alter the Fermi surface and cause the failure of the rigid band model noted in reference 1. This change in the Fermi surface increases the level at which the d-band is filled to x equal to 0.55. At 4.2 K, using the covalent bond picture, the hydrogen ions are screened from the conduction electrons by the highly localized palladium d-band for x between zero and 0.36. The screening decreases as x increases from 0.36 to 0.55 resulting in a more rapid increase in ρ_x/ρ_0 . Also the screening effect of the d-band, observed for x less than 0.55, decreases as the temperature increases from 4.2 K. With no screening at all, we would expect the curves drawn through the data at 4.2 and 273 K to be similar in shape. In order to explain the peak and the subsequent decrease as x approaches 1, two interpenetrating face-centered cubic lattices (NaCl lattice structure) are assumed with vacancies in the hydrogen lattice being filled as hydrogen is absorbed. This would give rise to a periodic lattice potential and decreasing resistance as x approaches 1.

The theoretical curve for the PdD_x system was based on the assumption that $\rho_x/\rho_0 \simeq 1$ when $x = 1$. Recent findings tend to support this assumption for hydrogen. Extrapolation of the curves drawn in figures 3 and 4 suggests that ρ_x/ρ_0 may be 1 when x equals 1. Further support can be derived from the work of Baranowski and Wisniewski (ref. 12), which shows that ρ_x/ρ_0 equals 1.02 for a palladium specimen in equilibrium with hydrogen above 15 000 atmospheres ($1.5 \times 10^9 \text{ N/m}^2$). Calculations based on their work and ours imply that the H/Pd atom ratio in the palladium lattice was 0.95 (see the appendix). However, $\rho_{0.95}/\rho_0$ at 1 atmosphere would probably be greater than 1.02,

since the resistivity of most metals decreases with increasing pressure (ref. 13). The model gives a satisfactory description for the shapes of the curves drawn through the hydrogen data at 4.2 and 273 K and for the differences in the slopes for x less than 0.7.

Results that are explained by screening effect concept. - Scatter is observed at 4.2 K that is due to variations in quench rate for x greater than 0.36 but not for x less than 0.36. We attribute some of this scatter to O-T transitions which occur down to at least x equal to 0.125 (refs. 4 and 6). The absence of this type of scatter for x less than 0.36, even though O-T transitions occur, can be ascribed to the screening effect. However, the effect of screening on the resistivity may be observed for higher values of x . Moreover, as the value of x is reduced from 0.55, the height of the resistivity peak in the resistivity against the temperature data near 50 K is drastically reduced (refs. 3 and 5). In fact, no peak has been observed for x less than 0.48. While the resistivity is primarily a measure of the electron scattering processes, specific heat measures the energy of the total system. Therefore, specific heat is not affected by screening, and specific heat peaks near 50 K have been observed for all values of x used. (Our observations on changes in ρ_x , for x approximately 0.90, below 50 K lead us to believe that O-T transitions occur for all values of x in which the β -phase is present. It seems that the observed time dependency for O-T transitions may be a function of x .)

In addition, the similarity in the ρ_x/ρ_0 values for both PdD $_x$ and PdH $_x$ where x is less than 0.36 can also be attributed to screening. Thus, it appears that where screening is dominant the resistivity is almost independent of the hydrogen isotope or its location in the palladium lattice.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 24, 1969,
129-03.

APPENDIX - ESTIMATION OF HYDROGEN-PALLADIUM ATOM RATIO OF PALLADIUM IMMERSSED IN HYDROGEN AT HIGH PRESSURE

Baranowski and Wisniewski (ref. 12) show that R/R_0 (the resistance ratio at room temperature) equals 1.02 for palladium immersed in hydrogen at the highest pressure they reported. This was above 16 000 atmospheres (1.6×10^9 N/cm²). No values were given for the hydrogen content of their specimens when the resistance was measured. Because ρ_x/ρ_0 (which is the same as R/R_0) is known as a function of hydrogen content of palladium (fig. 3), we can estimate the hydrogen content of the Baranowski and Wisniewski specimens in the region where our ρ_x/ρ_0 data overlap their R/R_0 data. There may be some error due to the difference in temperature at which the two sets of data were obtained. However, no other data are currently available.

It has been shown that (ref. 7)

$$\frac{H}{Pd} = 0.69 + \frac{\ln p}{b}$$

where p is pressure and b is a constant. By substituting the values of H/Pd and the corresponding values of p in this equation, the value of b can be estimated (see table I).

TABLE I. - DATA FOR ESTIMATION OF "b"

Resistivity ratio, ρ_x/ρ_0	Hydrogen-palladium atom ratio from fig. 3, H/Pd	Hydrogen pressure, $\ln p_H$ (a)	Constant, b
1.35	0.935	8.84	36.1
1.40	.925	8.54	36.3
1.50	.905	7.92	36.8
1.60	.880	7.19	<u>37.8</u>
			Average 36.8

^aThese values of $\ln p_{H_2}$ were obtained by using a curve prepared by plotting p_{H_2} against $\log a_{H_2}$ data taken from the figure given in reference 4.

Upon substituting the average value of b and 16 500 atmospheres for the highest pressure indicated on their curve, an x of 0.95 is obtained.

REFERENCES

1. Bambakidis, Gust; Smith, Robert J.; and Otterson, Dumas A.: Electrical Resistivity as a Function of Deuterium Concentration in Palladium. NASA TN D-4970, 1968.
2. Smith, Robert J.: Anomalous Electrical Resistivity of Palladium-Deuterium System Between 4.2° and 300° K. NASA TN D-2568, 1965.
3. Schindler, A. I.; Smith, R. J.; and Kammer, E. W.: Low Temperature Dependence of the Electrical Resistivity and Thermoelectric Power of Palladium and Palladium-Nickel Alloys Containing Absorbed Hydrogen. Proceedings of the Tenth International Congress on Refrigeration. Vol. I. Pergamon Press, 1960, pp. 74-79.
4. Ferguson, G. A., Jr.; Schindler, A. I.; Tanaka, T.; and Morita, T.: Neutron Diffraction Study of Temperature-Dependent Properties of Palladium Containing Absorbed Hydrogen. Phys. Rev., vol. 137A, no. 2, Jan. 18, 1965, pp. 483-487.
5. Haywood, C. T.; and Verdini, L.: Electrical Resistivity Measurements in Palladium-Hydrogen Alloys. Can. J. Phys., vol. 46, no. 18, Sept. 15, 1968, pp. 2065-2071.
6. Aston, J. G.; and Mitacek, P.: Solutions of Hydrogen in Palladium. Non-Stoichiometric Compounds. Advances in Chemistry Series Number 39, American Chemical Society, 1963, pp. 111-121.
7. Barton, J. C.; and Lewis, F. A.: Overvoltage and Hydrogen Content of Palladium Cathodes. Zeit fur Phys. Chem. N.F., vol. 33, 1962, pp. 99-110.
8. Lewis, F. A.: The Palladium Hydrogen System. Academic Press, 1967.
9. Andrews, J. N.; and Ubbelohde, A. R.: Overvoltage and Diffusion Through Iron and Palladium. Proc. Royal Soc. (London), Ser. A, vol. 253, no. 1272, Nov. 17, pp. 6-15.
10. Smialowski, Michael: The Action of Cathodically Evolved Hydrogen on Iron and Nickel as Special Cases of Corrosion-Embrittlement of Metals. Chem. & Ind., Aug. 1959, pp. 1078-1083.
11. Vuillemin, Joseph J.: De Haas - van Alphen Effect and Fermi Surface in Palladium. Phys. Rev., vol. 144, no. 2, Apr. 15, 1966, pp. 396-405.
12. Baranowski, B.; and Wisniewski, R.: The Electrical Resistance of Palladium at High Pressures of Gaseous Hydrogen at Room Temperature. J. Phys. Chem. Solids, vol. 29, 1968, pp. 1275-1276.
13. Mott, N. F.; and Jones, H.: The Theory and Properties of Metals and Alloys. Dover Publ., Inc., 1958, p. 271.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546
OFFICIAL BUSINESS

FIRST CLASS MAIL



POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

000 001 51 51 3DS 69255 00903
AIR FORCE WEAPONS LABORATORY/WL1L1/
KIRTLAND AIR FORCE BASE, NEW MEXICO 8711

ATTN: LEO BEYMAN, CHIEF, TECH. LIBRARY

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546